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An Ellipsometric Measurement of Optical Properties for InP Surfaces

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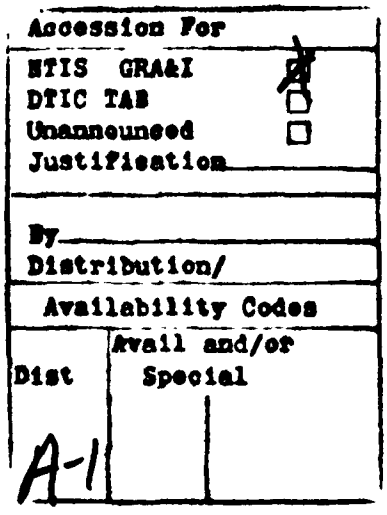

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Abstract

Several chemical cleaning procedures for InP surfaces have been studied using ellipsometry. The strong influence of cleaning on the optical properties of InP surfaces suggests that the measurements involve the formation of surface films. In order to determine the complex index of refraction for InP, a novel method which employs ellipsometry measurements of a thin non-absorbing film on a substrate rather than measurements of a bare surface has been explored. From the knowledge of the refractive index for a series of thicknesses of films on a substrate, the complex refractive index value for the substrate can be determined. Plasma Enhanced Chemical Vapor Deposition (PECVD) SiO_2 and Si_3N_4 films on InP have been used for this experiment, and the complex refractive index for InP has been determined to be 3.521+i0.300 at the wavelength of 632.8 nm.

Introduction

Surface preparation has been shown to have a significant influence on the optical properties of a semiconductor surface(1,2). Chemically reactive Si, Ge, and III-V semiconductors form a native oxide layer upon exposure to air(3,4). Therefore, an abrupt ambient-substrate boundary is practically unachievable with these surfaces except for a short time with the surfaces in an ultra high vacuum. Recently, it has been shown by in-situ ellipsometry and in-situ contact angle measurements(5) that chemical cleaning left some residue film on Si surfaces. Detailed ex-situ ir spectroscopy studies indicate that the film may be H terminated Si(6,7). All these facts imply that the literature discrepancy of the reported optical properties of Si, Ge, and the compound semiconductors could be interpreted in terms of different surfaces being measured, i.e. a different surface film on a substrate despite cleaning.

The widely cited values of the complex refractive index of InP in the uv-visible spectral region were obtained from Kramers-Kronig analysis of reflectance measurements by Cardona(8,9). These values are lower than those determined ellipsometrically by Aspnes and Studna(10). Recently, we have examined the InP optical constants at the wavelength 632.8 nm. A discrepancy as large as three percent has been found in the real and ten percent in the imaginary part of the complex index which results in about one degree difference in the ellipsometric variables Ψ and Δ,

where Ψ is the change in the amplitude ratio, and Δ is the change in phase difference of polarized light upon reflection from a sample surface.

Due to the high accuracy and the versatile ambient compatibility, ellipsometry has been used to measure the optical properties of semiconductor surfaces(11,12). However, the reported measurements on InP substrates involve, more or less, the dielectric properties of a surface film, which inevitably exists if the sample is not cleaned and kept in a high vacuum system(13-15). Unlike the previous studies, we did not try to eliminate the InP surface layer, instead we measured the surface coated with a thin PECVD film. Taking advantage of the weak dependence of the Ψ and Δ on the film refractive index when the film thickness is less then 20 nm, and even without knowing an accurate value for the film index, the complex refractive index for InP at 632.8 nm was determined with high accuracy by fitting the ellipsometrically measured Ψ-Δ pairs of a series of thicknesses of thin films on the substrate.

It is intended, in this paper, to report the observations of the influence of different chemical treatments on the optical properties of InP, to describe the idea and the experimental results from the novel method for determining the complex index for InP, and to compare our results with literature values.

Experimental Procedures

Commercially available, polished, N-type Sn-doped, (100) oriented InP wafers($n=2x10^{18}cm^{-3}$) were used in the surface cleaning experiments. The wafers were cut into 1 cm^2 pieces. The pretreatments of the InP samples are summarized in Table 1. Group 1 samples were exposed to a 5 minute boiling degrease in tetrachloroethylene, then rinsed in the mixture of acetone and methanol for about 10 minutes, followed by another 10 minute rinsing in acetone, and blown dry by compressed N_2 gas(16). For convenience, the Group 1 cleaning procedure is called "degreasing". Group 2 samples first received the degreasing, then a 10 second concentrated HF dip, deionized water, d.i., rinse, and N_2 blow dry. Group 3 samples were cleaned in the way similar to that of the Group 2 samples. However, instead of HF dip and d.i. water rinse, a chemi-mechanical polishing in a 1% Br_2/methanol solution and methanol rinse were employed. Group 4 samples were cleaned in the sequence of degreasing, HF dip, d.i. water rinse, 1% Br_2/methanol polish, methanol rinse, and N_2 dry. Immediately after the chemical cleaning, two ellipsometry measurements were made in the laboratory ambient on different surface spots for each sample.

A manual high precision ellipsometer was used for the measurements. A He-Ne laser was used to provide a stable, highly collimated, monochromatic light beam. A modified McCrackin procedure was applied for the ellipsometer alignment(17). In the alignment procedure, first the optical bench of the ellipsometer was autocollimated, and then the laser and the optical

components, i.e., polarizer, compensator, and analyzer, were positioned on the optical axis defined in the autocollimation step. Finally the optical components were calibrated. The full procedure enabled the azimuth angles of the components as well as the incident angle to be known to 0.01^0. A 70.00^0 incident angle was used, and two-zone measurements were employed through out our work, in order to obtain high accuracy(18).

N-type undoped (100) oriented InP wafers($n<10^{16}cm^{-3}$), and P-type B-doped (100) Si wafers were used for the remote PECVD of SiO_2 and Si_3N_4 films. Before the samples were loaded into the deposition chamber, the InP samples were cleaned as Group 2 samples described above, and Si samples were given a modified RCA cleaning(19). For each run, one InP and three Si samples were loaded on the sample stage, which was heated to 250^0C during the deposition. The pressure of the PECVD chamber was 80 mtorr, and the power was 30 watts. For the SiO_2 deposition, a 300/100 sccm Ar/O_2 gas flow was used to generate the plasma, and 5 sccm SiH_4 was supplied as the Si source. For silicon nitride deposition, a 400/10 sccm Ar/N_2 gas flow was used for plasma generation, and 5/100 sccm SiH_4/N_2 was supplied in the deposition chamber. Two spots on each of these PECVD samples were ellipsometrically measured, and the average value for each sample was used in the data analysis.

Results and Discussion

An ideal optically isotropic ambient-film-substrate, three

phase, optical model is adequate for our ellipsometry data analysis(20). In the model, the measured Ψ and Δ are related to the optical properties of the system investigated by the relation

$$\tan \Psi \exp(j\Delta) = \rho(N_0, N_1, N_2, L, \phi, \lambda)$$

where N_0, N_1, and N_2 are the complex indices of the ambient, the surface film, and the substrate, respectively. L is the film thickness, ϕ is the angle of the incident beam, and λ is the incident radiation wavelength. With the N_0, ϕ and λ as experimentally controlled variables, and with N_2 fixed, any change in the measured Ψ and Δ reflects a change in the film index N_1 and the film thickness L.

The measured Ψ and Δ values for InP are strongly dependent on the surface chemical treatments, as shown in Table 2. The degreasing of InP in hot tetrachloroethylene, Group 1 samples, altered surface properties, with both Ψ and Δ slightly lower than the values of the as-received InP surface, as listed in the first row under no clean category. The measured Ψ, Δ values were analyzed using a non-absorbing film on an absorbing substrate model to yield a film thickness and refractive index, and these values are in the last two columns of Table 2. In the analysis, 3.536+i0.307 was used for the complex refractive index of InP substrates(10). The small change due to degreasing could be accounted for by the index change of the surface film due to the exposure to the solvents. The HF dip of the Group 2 samples resulted in a further decrease in Ψ but an increase in Δ. This

indicated that the thickness of the surface layer was reduced a ng with, perhaps, a slight change in film index. The 10 second HF dip removed approximately 1.0 nm of the film. The Group 3 samples, which received the Br_2 methanol polishing, showed a large change in Ψ and Δ. The surface yielded the highest Δ value, thus the lowest film thickness. The cleaning sequence of degreasing, HF dipping, and Br_2 methanol polishing, Group 4 samples, gave the lowest Ψ value.

In order to circumvent the above described difficulty of the influence of the cleaning procedure with the measurement of N_1, we used non-adventitious PECVD films with known properties and with an adjusted film thickness to maximize the sensitivity to the InP substrate. The measured Ψ and Δ of the PECVD SiO_2 films on Si substrates are shown in Figure 1. The solid line was calculated by assuming a particular film index while varying the film thickness, while the value of 3.865+i0.018 was used for the complex index of Si substrate(21,22), and the two dashed lines were derived from two other film index values. From the Figure, the index of the SiO_2 films on Si was determined as 1.39+i0.00, with an uncertainty of about ±0.05. The deposition temperature of 250^{0}C and a remote plasma source were used, in order to minimize the substrate damage during the deposition process. Therefore, it was assumed that the SiO_2 films deposited on Si and InP, which were side-by-side in the plasma chamber, have the same optical properties. The assumption enabled the index value,

1.39+i0.00, obtained from the PECVD SiO_2 films on Si to be used for the analysis of the same films on InP. Figure 2 shows the measured Ψ-Δ pairs for SiO_2 films on InP, and the simulated curves using different complex indices for InP while varying the SiO_2 film thickness. The top dashed curve was calculated by using Aspnes' index value 3.536+i0.307 for the InP substrate(10), while the bottom dashed curve came from the Cardona's value of 3.420+i0.278(8). The solid curve with a substrate index value 3.521+i0.300 gave the best fit to all the measured Ψ-Δ data points. The accuracy of this procedure can be simply estimated. The total experimental error was less than 0.02^0 in the measured Ψ and less than 0.05^0 in Δ. A deviation of 0.003 from the real part of the complex index or 0.004 from the imaginary part could independently cause more than 0.02^0 difference in the calculated Ψ, and 0.10^0 in the calculated Δ. To be conservative, the complex index could be represented as (3.521±0.003)+i(0.300 ±0.004). As mentioned above, there was about ±0.05 uncertainty in the index value for the SiO_2 films, however, this uncertainty did not affect the accuracy of our final result. As seen in Figure 3, the three curves correspond to surface films on InP with indices of 1.34+i.00, 1.39+i0.00, and 1.44+i0.00. As the film thickness goes below 10 nm, all the curves converge into a single one, with a deviation smaller than the measurement uncertainty of our ellipsometry hardware. The convergence ensures that the index value of InP could be determined

accurately, even the film index near the origin could be determined reasonably accurately.

Similarly, the index of the PECVD Si_3N_4 films on Si was determined as 1.70+i0.00. Again this value was adopted for the nitride films on InP. Using the procedure described above, the complex index of InP was determined as 3.521+i0.300, which is the same as that determined by using SiO_2 films. The experimental Ψ and Δ data and the simulated curves for the nitride films on InP are shown in Fig.4.

Figure 5 shows the calculated Ψ and Δ curves for SiO_2 and Si_3N_4 on InP using 3.521+i0.300 for the InP while varying film thicknesses. The measured data for both SiO_2 and Si_3N_4 on InP almost perfectly fit the calculated curves. This provides a consistency check on this value for InP. Our complex index value is in good agreement with the Aspnes value(10), 3.536+i0.307, as was determined by the spectroscopic ellipsometry. Our index value is higher, both in the real and the imaginary part, than those determined by reflectance measurements(8). We, therefore, agree with the comment(10) that the Kramers-Kronig analysis of reflectance data could cause notable errors because the extrapolated reflectance data in the experimental unobtainable wavelength ranges were used in the integration.

Conclusions

We have demonstrated that the surface preparation of InP influences the measured optical properties of InP. The influence may be derived from the alteration of either the refractive index or the thickness of a surface layer by the chemical treatments. In order to understand the precise nature of these influences, an in-situ solution spectroscopic ellipsometry study, which could eliminate the ambient effect caused by the interaction of the surface with the ambient and provide information about the surface roughness, is needed and is underway. Among the InP cleaning procedures investigated, the 1% Br_2 in methanol chemi-mechanical polishing produces the thinnest surface layer.

The complex refractive index for InP has been determined to be 3.521+i0.300 by the novel procedure. The new method has two distinguishable advantages over the techniques applying direct measurements of a bare surface. The measurements of a surface covered with a thin film eliminate the influence of the surface preparation, thus a reliable and reproducible result could be expected. The second advantage is that the weak dependence of Ψ and Δ on the film index relieves the requirement for having an accurate index value for the film. Therefore, the uncertainty of the final result is greatly reduced. The ellipsometric method described herein is generally applicable for other solid state materials.

Acknowledgement

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List of Tables

Table 1

Group	Cleaning Procedure
1	"degreasing"--- 5 min in hot tetrachloroethylene, 10 min in 1:1 acetone:methanol, 10 min in acetone, N_2 dry.
2	degreasing, 10 second concentrated HF dip, d.i. water rinse, N_2 dry.
3	degreasing, 1% Br_2 in methanol chemi-mechanical polish, methanol rinse, N_2 dry.
4	degreasing, 10 second HF dip, d.i. water rinse, 1% Br_2 in methanol polish, methanol rinse, N_2 dry.

Table 2

Sample Preparation	Ψ (^{0})	Std.Dev. (±)	Δ (^{0})	Std.Dev. (±)	Thickness (nm)	Refractive Index
No Clean	8.553	0.003	155.808	0.11	2.5	1.30
Group 1	8.495	0.09	155.254	0.80	1.8	1.75
Group 2	8.343	0.03	157.511	0.22	1.1	2.30
Group 3	8.314	0.14	158.938	0.56	0.7	2.40
Group 4	8.308	0.05	157.695	0.50	1.0	2.40

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Figure 1: The experimental and simulated Ψ and Δ data for PECVD SiO_2 films on Si substrates. The complex refractive index value for Si used in the simulations is 3.865+i0.018, and N_1 is the film refractive index. The top most point on each simulated curve corresponds to a bare Si surface, while the point on the other end of a curve represents a 25 nm film on Si.

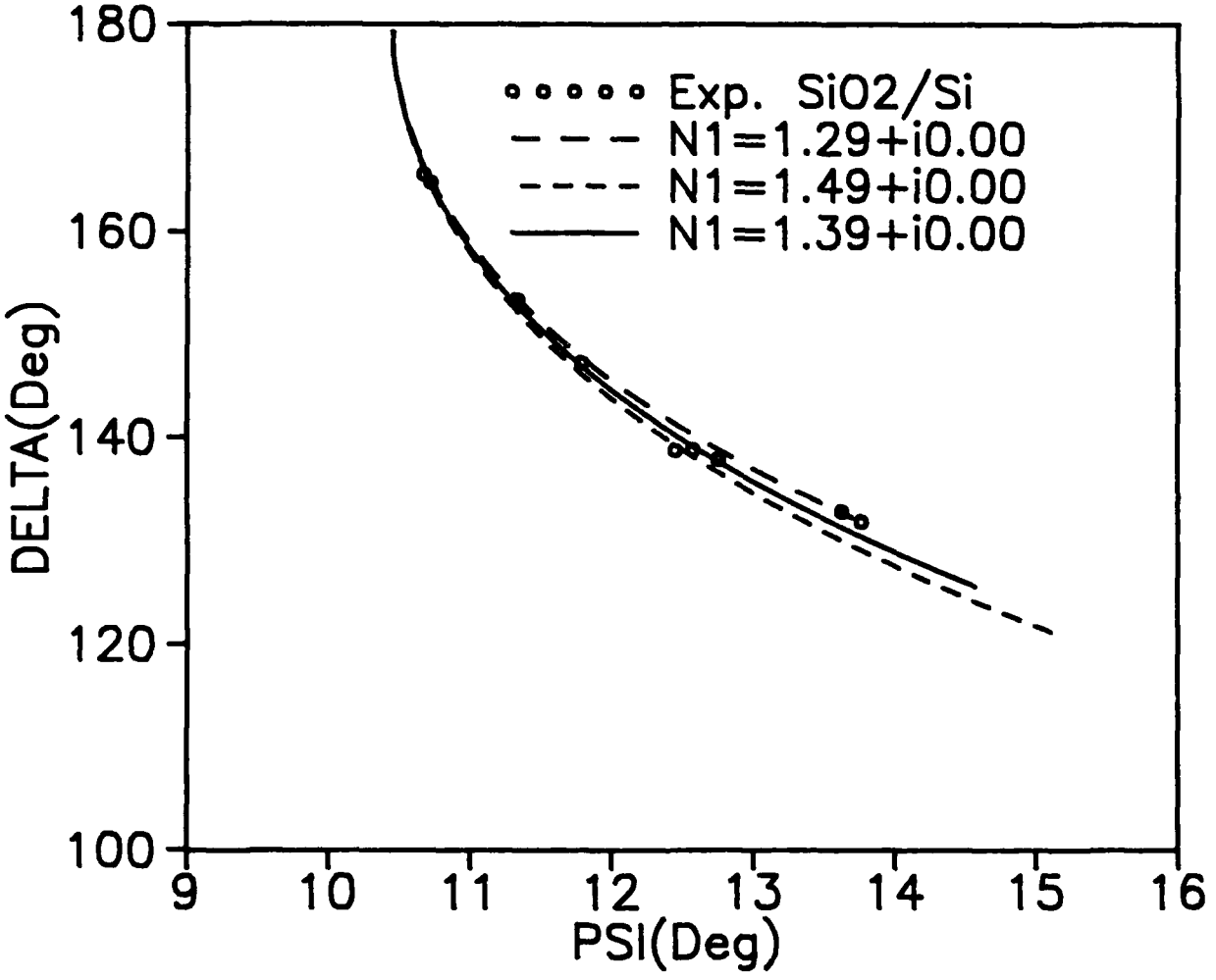
Figure 2: The simulated and experimental Ψ and Δ for silicon dioxide on InP. The film index used is N_1=1.39+i0.00, and N_2 is the complex index for InP. The dots are the measured Ψ and Δ which fit the simulated curve with N_2=3.521+i0.300.

Figure 3 : The calculated Ψ and Δ curves for films with an index of 1.34+i0.00, 1.39+i0.00, and 1.44+i0.00 on InP. The index of InP used is 3.521+i0.300. For each curve, the top most point corresponds a bare InP surface, and the point on the other end represents a 30 nm film.

Figure 4: The simulated Ψ and Δ and experimental Ψ-Δ pairs for silicon nitride film on InP. The film index used is 1.70+i0.00. N_2 is the complex refractive index for InP substrate. The solid curve with a substrate index of 3.521+i0.300 fits all the experimental data.

Figure 5: The measured Ψ-Δ for PECVD silicon dioxide and silicon nitride films on InP and the simulated curves. The index value 3.521+i0.300 is used for InP substrate, 1.39+i0.00 for silicon dioxide, and 1.70+i0.00 for silicon nitride.

Figure 1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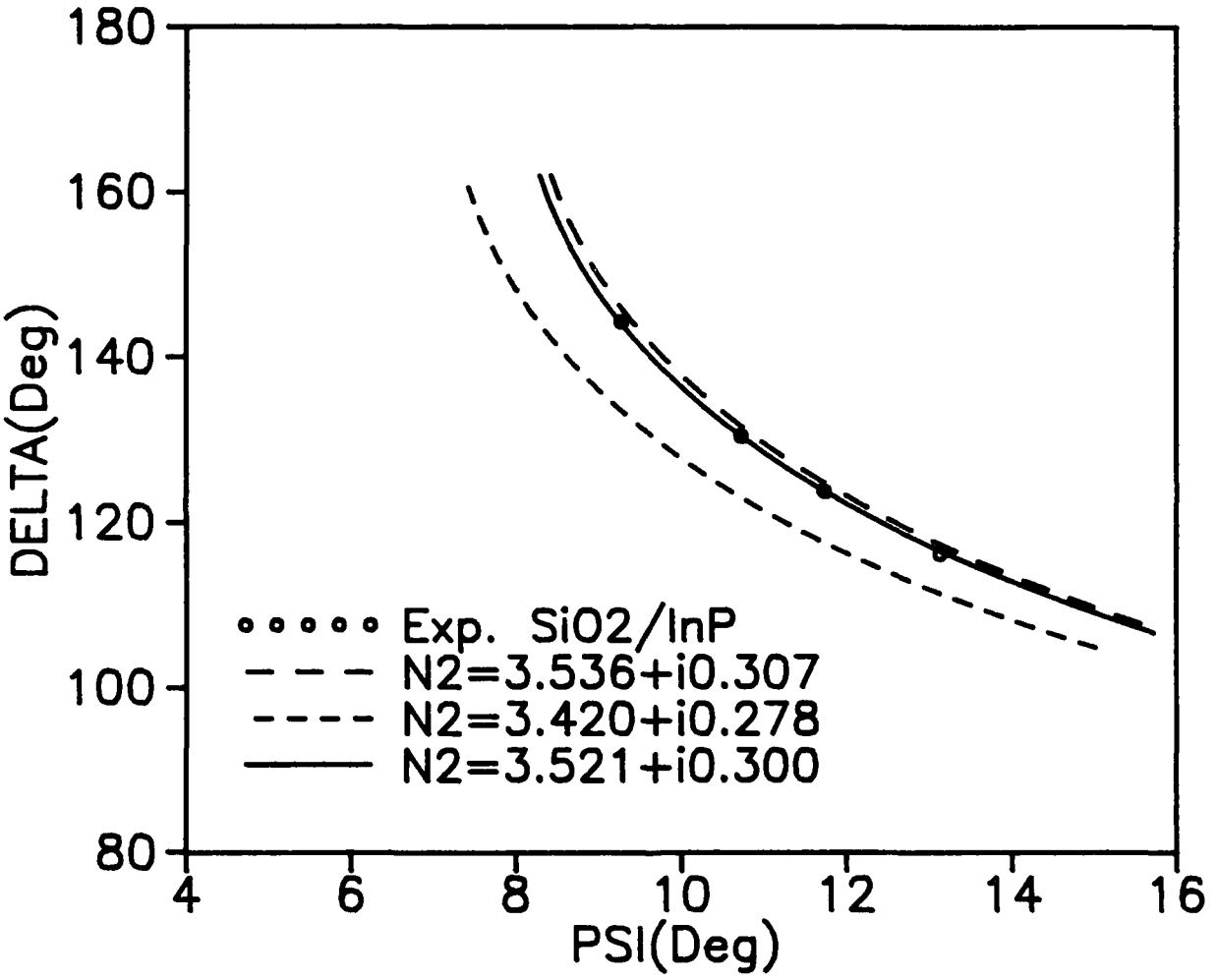
PSI(Deg)
Exp. SiO2/Si
N1=1.29+i0.00
N1=1.49+i0.00
N1=1.39+i0.00

Figure 2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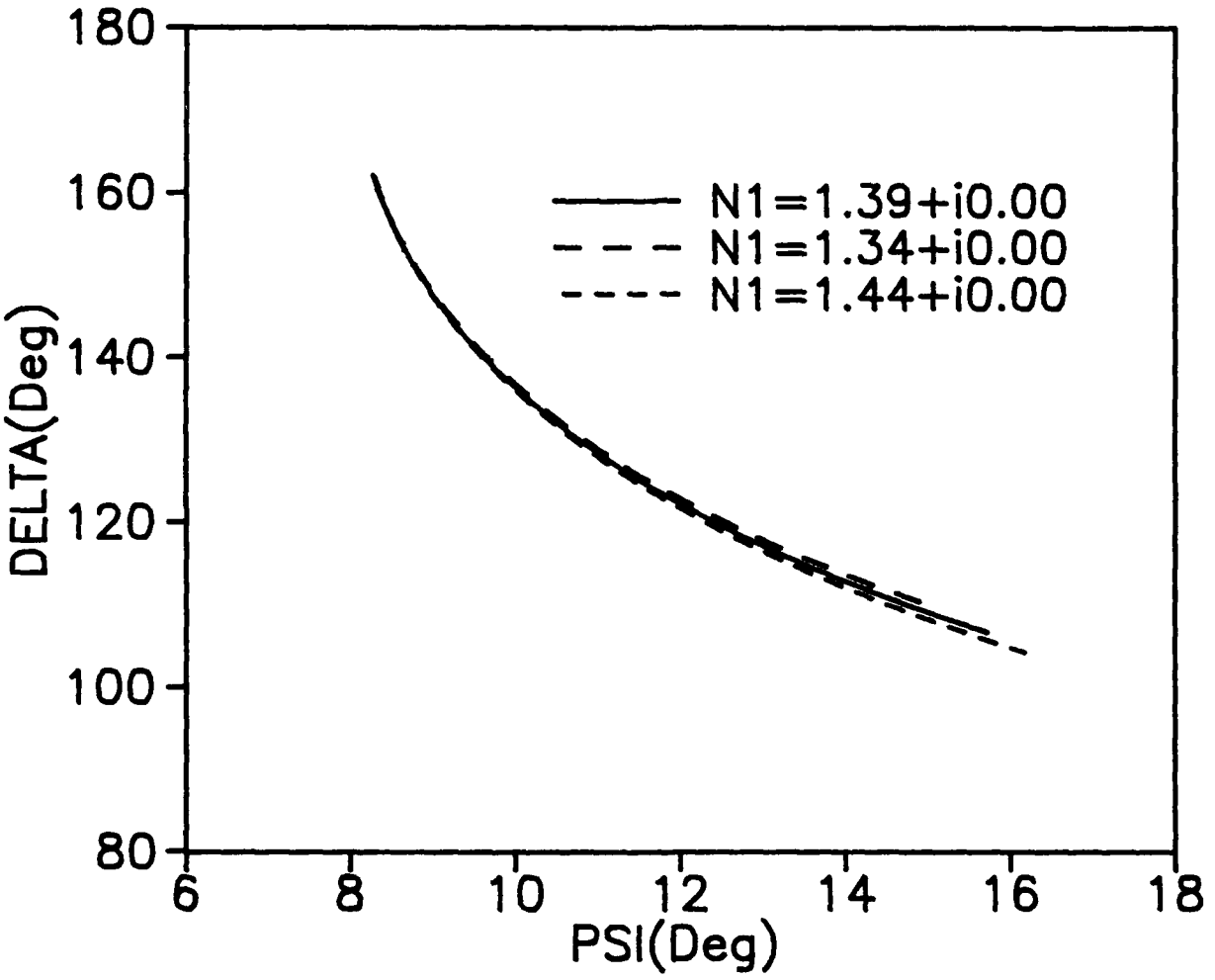
PSI(Deg)
Exp. SiO2/InP
N2=3.536+i0.307
N2=3.420+i0.278
N2=3.521+i0.300

Figure 3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N1=1.34+i0.00
N1=1.44+i0.00

Figure 4

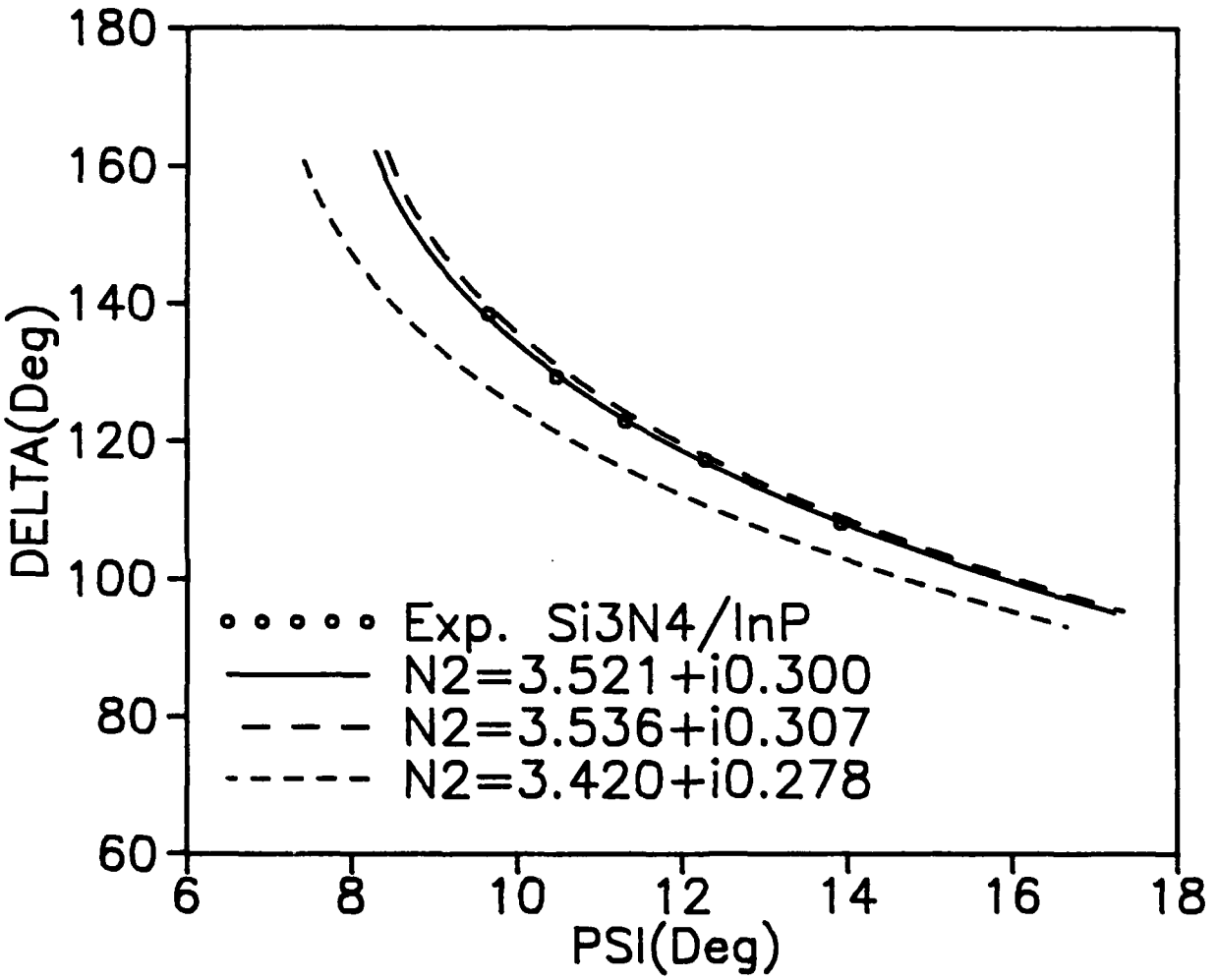
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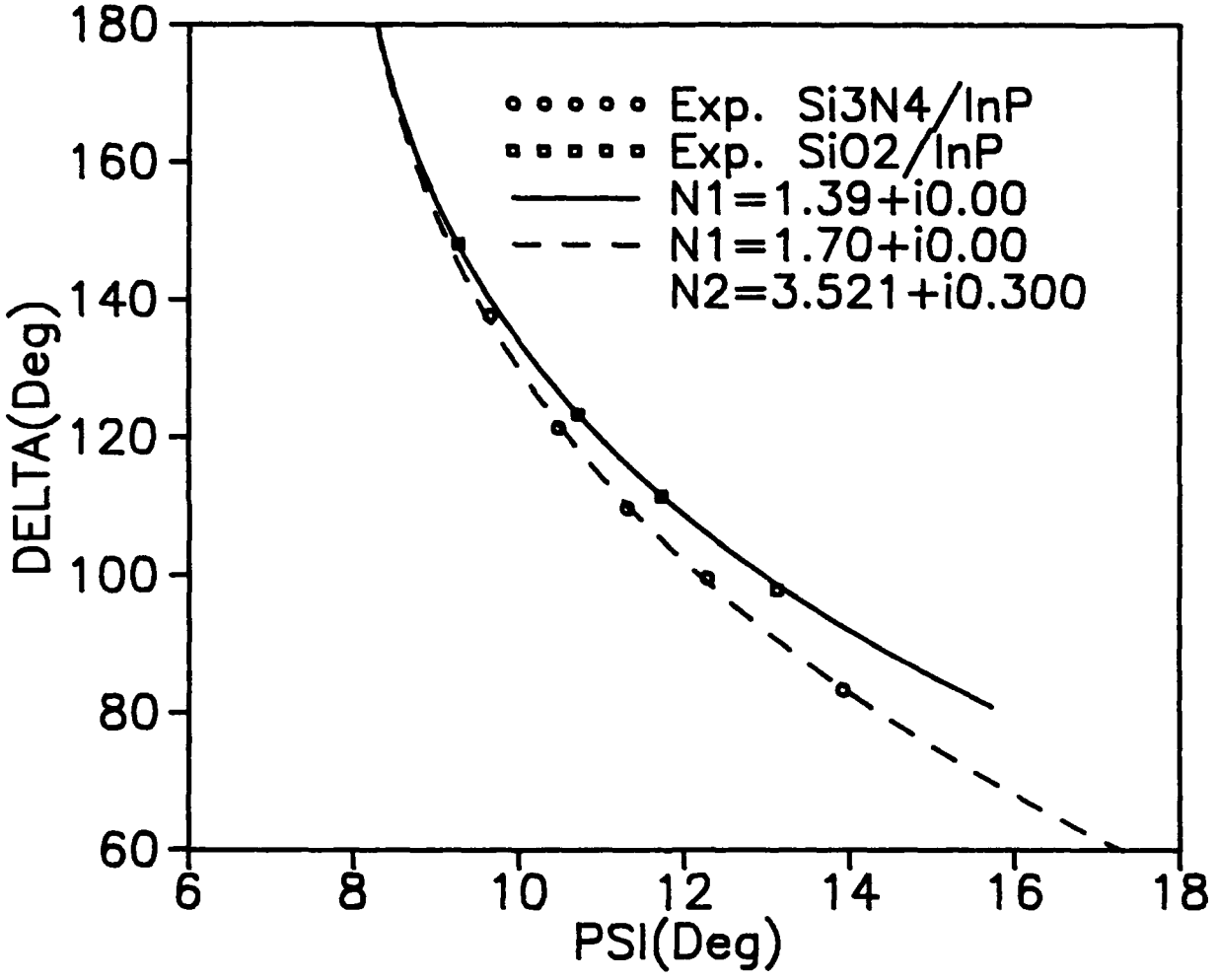
Figure 5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